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Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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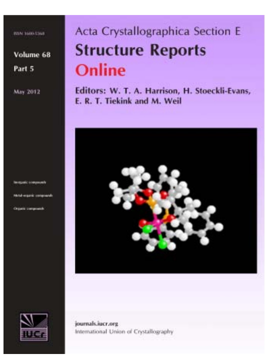
Acta Cryst. (2014). E**70**, i30



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$Na_{4.25}Mo_{15}S_{19}$: a novel ternary reduced molybdenum sulfide containing Mo_6 and Mo_9 clusters

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Received 21 May 2014; accepted 23 May 2014

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Mo–S) = 0.001 Å; disorder in solvent or counterion; R factor = 0.030; wR factor = 0.079; data-to-parameter ratio = 22.7.

The structure of tetrasodium pentadecamolybdenum nonadecasulfide, $Na_{4.25}Mo_{15}S_{19}$, is isotypic with $Na_{3.9}Mo_{15}Se_{19}$ [Salloum *et al.* (2013). *Acta Cryst.* E**69**, i67–i68]. It is characterized by $Mo_6S^i_8S^a_6$ and $Mo_9S^i_{11}S^a_6$ (where i represents inner and a apical atoms) cluster units that are present in a 1:1 ratio. The cluster units are centered at Wyckoff positions 2b and 2c, and have point-group symmetry $\overline{3}$ and $\overline{6}$, respectively. The clusters are interconnected through additional Mo—S bonds. The Na^+ cations occupy interunit voids formed by six or seven S atoms. One Mo, one S and one Na site [occupancy 0.751 (12)] are situated on mirror planes, and two other S atoms and one Na site (full occupancy) are situated on threefold rotation axes.

Related literature

For previous reports on the crystal structure of the $In_{\sim3}Mo_{15}Se_{19}$ compounds, see: Grüttner *et al.* (1979). For physical properties of this type of compounds, see: Seeber *et al.* (1979). The crystal structures of the substituted selenides $Ho_{0.76}In_{1.68}Mo_{15}Se_{19}$ and $In_{0.87}K_2Mo_{15}Se_{19}$ were reported by Salloum *et al.* (2006; 2007). For the isotypic sulfides $In_{3.7}Mo_{15}S_{19}$, $In_{1.6}Rb_2Mo_{15}S_{19}$, $In_{2.2}CsMo_{15}S_{19}$, $ScTl_2Mo_{15}S_{19}$ and $Na_{3.9}Mo_{15}Se_{19}$, see: Salloum *et al.* (2004*a*,*b*, 2013) and for $V_{1.42}In_{1.83}Mo_{15}Se_{19}$, see: Gougeon *et al.* (2010). For details of the *i*- and *a*-type ligand notation, see: Schäfer & von Schnering (1964).

Experimental

Crystal data

$Na_{4.25}Mo_{15}S_{19}$
M_r = 2145.95
Hexagonal, $P6_3/m$
a = 9.5340 (1) Å
c = 18.9803 (3) Å
V = 1494.11 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 7.44 mm^{-1}
T = 293 K
0.18 × 0.14 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: analytical (de Meulenaar & Tompa, 1965)
T_{min} = 0.363, T_{max} = 0.591
16576 measured reflections
1500 independent reflections
1322 reflections with $I > 2\sigma(I)$
R_{int} = 0.085

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.079
S = 1.13
1500 reflections
66 parameters
$\Delta\rho_{max}$ = 1.51 e Å^{-3}
$\Delta\rho_{min}$ = −1.85 e Å^{-3}

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

Intensity data were collected on the Nonius KappaCCD X-ray diffactometer system at the Centre de diffractométrie de l'Université de Rennes I (www.cdifx.univ-rennes1.fr).

Supporting information for this paper is available from the IUCr electronic archives (Reference: RU2060).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bergerhoff, G. (1996). *DIAMOND*. University of Bonn, Germany.
Duisenberg, A. J. M. (1998). PhD thesis, University of Utrecht, The Netherlands.
Gougeon, P., Gall, P., Salloum, D. & Potel, M. (2010). *Acta Cryst.* E**66**, i73.
Grüttner, A., Yvon, K., Chevrel, R., Potel, M., Sergent, M. & Seeber, B. (1979). *Acta Cryst.* B**35**, 285–292.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* A**19**, 1014–1018.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands
Salloum, D., Gautier, R., Gougeon, P. & Potel, M. (2004*a*). *J. Solid State Compds*, **177**, 1672–1680.
Salloum, D., Gougeon, P. & Gall, P. (2013). *Acta Cryst.* E**69**, i67–i68.
Salloum, D., Gougeon, P. & Potel, M. (2006). *Acta Cryst.* E**62**, i83–i85.
Salloum, D., Gougeon, P. & Potel, M. (2007). *Acta Cryst.* E**63**, i8–i10.
Salloum, D., Gougeon, P., Roisnel, T. & Potel, M. (2004*b*). *J. Alloys Compd*, **383**, 57–62.
Schäfer, H. & von Schnering, H. G. (1964). *Angew. Chem.* **76**, 833–845.
Seeber, B., Decroux, M., Fisher, Ø., Chevrel, R., Sergent, M. & Grüttner, A. (1979). *Solid State Commun.* **29**, 419–423.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2014). E**70**, i30 [doi:10.1107/S160053681401201X]

$Na_{4.25}Mo_{15}S_{19}$: a novel ternary reduced molybdenum sulfide containing Mo_6 and Mo_9 clusters

D. Salloum, P. Gougeon and P. Gall

1. Comment

The reduced molybdenum compounds $In_{3+x}Mo_{15}X_{19}$ (X = S, Se) (Grüttner *et al.*, 1979; Salloum *et al.*, 2004*a*) crystallize in an interesting structural type characterized by an equal mixture of Mo_6 and Mo_9 clusters and by In atoms that occupy two or three different crystallographically positions depending on their formal oxidation state of +1 or +3. Subsequently, isomorphous compounds such as $Ho_{0.76}In_{1.68}Mo_{15}Se_{19}$ (Salloum *et al.*, 2006), $In_{0.87}K_2Mo_{15}Se_{19}$ (Salloum *et al.*, 2007), $V_{1.42}In_{1.83}Mo_{15}Se_{19}$ (Gougeon *et al.*, 2010), $In_{3.7}Mo_{15}S_{19}$ (Salloum *et al.*, 2004*a*), $In_{1.6}Rb_2Mo_{15}S_{19}$, $In_{2.2}CsMo_{15}S_{19}$ and $ScTl_2Mo_{15}S_{19}$ (Salloum *et al.*, 2004*b*) have been synthesized. In the latter compounds, the Ho, V and Sc atoms replace the trivalent indium and the K, Cs, and Tl atoms the monovalent one. Recently, we described the crystal structure of $Na_{3.9}Mo_{15}Se_{19}$ (Salloum *et al.*, 2013) in which the sodium replaces the monovalent as well as the trivalent indium for the first time. We present here the sulfide analogue $Na_{4.25}Mo_{15}S_{19}$.

The Mo—S framework of the title compound consists of the cluster units $Mo_6S^i_8S^a_6$ and $Mo_9S^i_{11}S^a_6$ in a 1:1 ratio (for details of the i- and a-type ligand notation, see Schäfer & von Schnering (1964)). Both components are interconnected through additional Mo—Se bonds (Figs. 1 and 2). The first unit can be described as an Mo_6 octahedron surrounded by eight face-capping inner S^i and six apical S^a ligands. The Mo_9 cluster is surrounded by 11 S^i atoms capping one or two faces of the bioctahedron and six S^a ligands above the apical Mo atoms. The $Mo_6S^i_8S^a_6$ and $Mo_9S^i_{11}S^a_6$ units are centered at Wyckoff positions 2 b and 2c and have point-group symmetry $\overline{3}$ and $\overline{6}$, respectively. The Mo—Mo distances within the Mo_6 cluster are 2.6900 (5) Å for the distances of the Mo triangles formed by the Mo1 atoms related through the threefold axis, and 2.7098 (6) Å for the distances between these triangles. The Mo—Mo distances within the Mo_9 clusters are 2.6349 (5) and 2.6756 (7) Å in the triangles formed by the atoms Mo2 and Mo3, respectively, and 2.7081 (4) and 2.7303 (4) Å for those between the $Mo2_3$ and $Mo3_3$ triangles. All the latter Mo—Mo distances are closed to those observed in the selenide analogue indicating that the cationic charge transfer towards the Mo_6 and Mo_9 clusters are similar in both compounds. The S atoms bridge either one (S1, S2, S4 and S5) or two (S3) triangular faces of the Mo clusters. Moreover, atoms S1 and S2 are linked to an Mo atom of a neighboring cluster. The Mo—S bond distances range from 2.4184 (14) to 2.5624 (10) Å within the $Mo_6S^i_8S^a_6$ unit, and from 2.4033 (13) to 2.5947 (8) Å within the $Mo_9S^i_{11}S^a_6$ unit. In both cases, the shortest bonds involve the S4 and S5 terminal atoms and the longest ones correspond to the interunit Mo1—S2 and Mo2—S1 bonds. Each $Mo_9S^i_{11}S^a_6$ cluster is thus interconnected to six $Mo_6S^i_8S^a_6$ units (and *vice versa*) *via* Mo2—S1 bonds (and Mo1—S2 bonds, respectively), forming the three-dimensional Mo—S framework, the connective formula of which is $Mo_9S^i_5S^{i\text{-}a}_{6/2}S^{a\text{-}i}_{6/2}$, $Mo_6S^i_2S^{i\text{-}a}_{6/2}S^{a\text{-}i}_{6/2}$. It results from this arrangement that the shortest intercluster Mo1—Mo2 distance is 3.5202 (6) Å, indicating only weak metal-metal interactions between the Mo clusters. The $Na1^+$ cations are surrounded by seven S atoms forming a distorted tricapped tetrahedron. The S5 and S2 atoms forming the tetrahedron are at 2.699 (5) and 3.1669 (13) Å from the Na1 atom, and the capping S1 atoms are at 3.3609 (19) Å. The $Na2^+$ cations occupy partially at 75.1% a triangular group of distorted octahedral cavities around the threefold axis, which are formed by two $Mo_6S^i_8S^a_6$ and three $Mo_9S^i_{11}S^a_6$ units. The Na2—S distances are in the 2.538 (4) - 3.055 (4) Å range.

2. Experimental

Single crystals of $Na_{4.25}Mo_{15}S_{19}$ were prepared from an ion exchange reaction on single crystals of $In_{3+x}Mo_{15}S_{19}$ with an excess of NaI at 1073 K. The mixture was sealed under vacuum in a long silica tube. The end of tube containing the crystals of $In_{3+x}Mo_{15}S_{19}$ and InI was placed in a furnace with about 5 cm of the other end out from the furnace, at about the room temperature. The furnace was heated at 1073 K for 48 h. After reaction, crystals of InI were observed at the cool end of the tube. The black crystals of the title compound were subsequently washed with water to remove the excess of InI. Qualitative microanalyses using a Jeol JSM 6400 scanning electron microscope equipped with a Oxford INCA energy- dispersive-type X-ray spectrometer did not reveal the presence of indium in the crystals and indicated roughly stoichiometries comprised between 3.8 and 4.4 for the Na content.

3. Refinement

No significant deviation from full occupancy was observed for Na1. The site occupation factor of Na2 was refined freely leading to the final stoichiometry $Na_{4.25\,(4)}Mo_{15}S_{19}$.

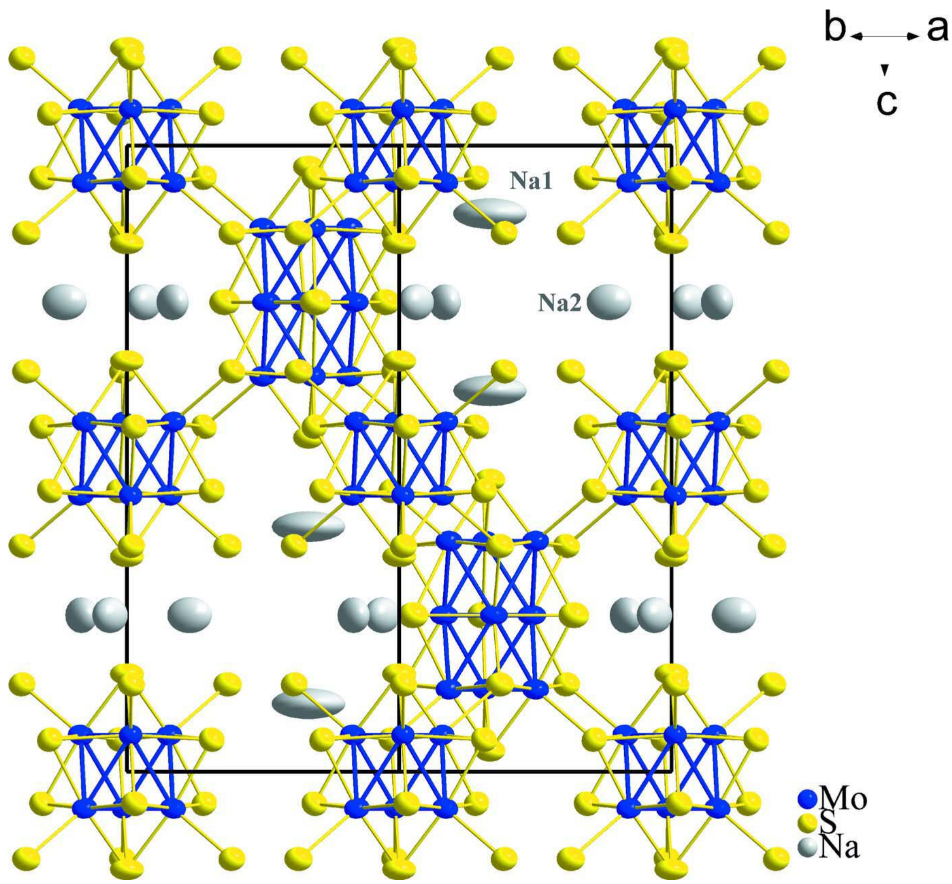

Figure 1

View of $Na_{4.25}Mo_{15}S_{19}$ along [110]. Displacement ellipsoids are drawn at the 97% probability level.

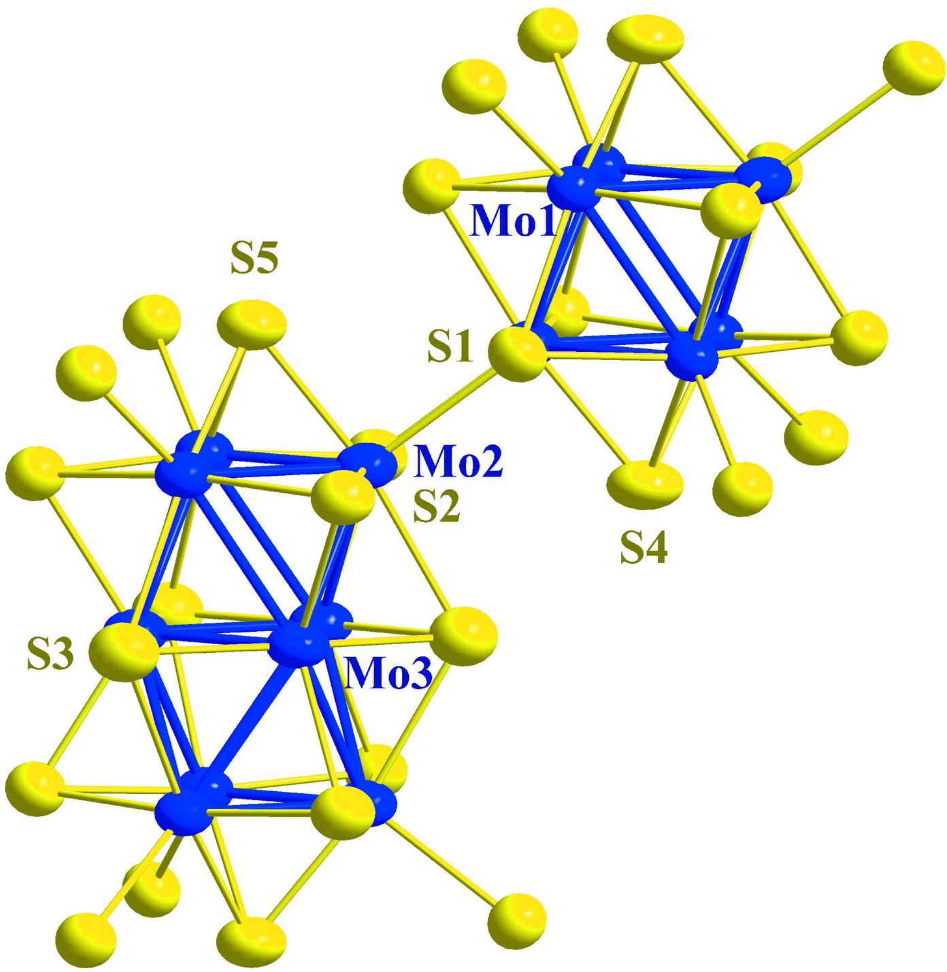

Figure 2

Plot showing the atom-numbering scheme and the interunit linkage of the $Mo_9S_{11}S_6$ and $Mo_6S_8S_6$ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

Tetrasodium pentadecamolybdenum nonadecasulfide

Crystal data

$Na_{4.25}Mo_{15}S_{19}$
M_r = 2145.95
Hexagonal, $P6_3/m$
a = 9.5340 (1) Å
c = 18.9803 (3) Å
V = 1494.11 (3) Å^3
Z = 2
F(000) = 1962
D_x = 4.770 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 16576 reflections
θ = 2.2–30.0°
μ = 7.44 mm^{-1}
T = 293 K
Multi-faceted crystal, black
0.18 × 0.14 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ scans (κ = 0) + additional ω scans
Absorption correction: analytical (de Meulenaar & Tompa, 1965)
T_{min} = 0.363, T_{max} = 0.591
16576 measured reflections
1500 independent reflections

1322 reflections with $I > 2\sigma(I)$
$R_{int} = 0.085$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.2°$
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 11$
$l = -22 \rightarrow 26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.079$
$S = 1.13$
1500 reflections
66 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 5.1576P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.51$ e Å^{-3}
$\Delta\rho_{min} = -1.85$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00266 (19)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Mo1	0.84424 (3)	0.01344 (3)	−0.058496 (18)	0.01072 (12)	
Mo2	0.50077 (4)	−0.18303 (4)	0.131678 (19)	0.01177 (12)	
Mo3	0.34797 (5)	−0.16448 (5)	0.2500	0.01301 (13)	
S1	0.71650 (10)	0.02755 (11)	0.05118 (5)	0.01268 (18)	
S2	0.36949 (11)	−0.01601 (11)	0.13948 (5)	0.01344 (19)	
S3	0.05126 (16)	−0.30754 (17)	0.2500	0.0171 (3)	
S4	0.0000	0.0000	−0.15617 (9)	0.0184 (3)	
S5	0.3333	−0.3333	0.03365 (9)	0.0156 (3)	
Na2	0.7703 (5)	−0.0623 (4)	−0.2500	0.0283 (12)	0.751 (12)
Na1	0.3333	−0.3333	−0.1085 (3)	0.0789 (17)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01252 (16)	0.01051 (16)	0.00816 (19)	0.00505 (11)	0.00061 (10)	−0.00031 (9)
Mo2	0.01434 (17)	0.01410 (17)	0.00778 (19)	0.00778 (12)	−0.00017 (10)	−0.00005 (10)
Mo3	0.0153 (2)	0.0159 (2)	0.0075 (2)	0.00754 (17)	0.000	0.000
S1	0.0121 (4)	0.0138 (4)	0.0121 (4)	0.0064 (3)	0.0013 (3)	0.0005 (3)
S2	0.0154 (4)	0.0143 (4)	0.0112 (4)	0.0079 (3)	0.0001 (3)	0.0008 (3)
S3	0.0185 (6)	0.0198 (6)	0.0133 (7)	0.0098 (5)	0.000	0.000
S4	0.0228 (5)	0.0228 (5)	0.0095 (8)	0.0114 (2)	0.000	0.000
S5	0.0187 (4)	0.0187 (4)	0.0093 (7)	0.0094 (2)	0.000	0.000
Na2	0.040 (2)	0.0256 (19)	0.026 (2)	0.0218 (16)	0.000	0.000

Na1	0.109 (3)	0.109 (3)	0.018 (2)	0.0547 (14)	0.000	0.000

Geometric parameters (Å, º)

Mo1—S4^{i}	2.4184 (14)	S2—Mo1^{iv}	2.5624 (10)
Mo1—S1	2.4492 (10)	S2—Na2^{iv}	2.781 (2)
Mo1—S1^{ii}	2.4565 (9)	S2—Na1^{iv}	3.1669 (13)
Mo1—S1^{iii}	2.4830 (9)	S3—Mo3^{viii}	2.4419 (14)
Mo1—S2^{iv}	2.5624 (10)	S3—Na2^{xi}	2.538 (4)
Mo1—Mo1^{v}	2.6900 (5)	S3—Mo2^{x}	2.5947 (8)
Mo1—Mo1^{vi}	2.6900 (5)	S3—Mo2^{viii}	2.5947 (8)
Mo1—Mo1^{iii}	2.7098 (6)	S3—Na2^{iv}	3.055 (4)
Mo1—Mo1^{ii}	2.7098 (6)	S4—Mo1^{xii}	2.4184 (14)
Mo1—Na2	3.7042 (8)	S4—Mo1^{xiii}	2.4184 (14)
Mo2—S5	2.4033 (13)	S4—Mo1^{viii}	2.4184 (14)
Mo2—S2	2.4733 (9)	S4—Na2^{xiii}	2.649 (3)
Mo2—S2^{vii}	2.5070 (9)	S4—Na2^{viii}	2.649 (3)
Mo2—S1	2.5429 (10)	S4—Na2^{xii}	2.649 (3)
Mo2—S3^{vii}	2.5947 (8)	S5—Mo2^{viii}	2.4033 (13)
Mo2—Mo2^{vii}	2.6349 (5)	S5—Mo2^{vii}	2.4033 (13)
Mo2—Mo2^{viii}	2.6349 (5)	S5—Na1	2.699 (5)
Mo2—Mo3^{vii}	2.7081 (4)	Na2—S3^{xiv}	2.538 (4)
Mo2—Mo3	2.7303 (4)	Na2—S4^{i}	2.649 (3)
Mo3—S3^{vii}	2.4419 (14)	Na2—S4^{xv}	2.649 (3)
Mo3—S3	2.4504 (14)	Na2—S2^{xvi}	2.781 (2)
Mo3—S2^{ix}	2.4810 (10)	Na2—S2^{iv}	2.781 (2)
Mo3—S2	2.4810 (10)	Na2—Mo3^{iv}	2.896 (3)
Mo3—Mo3^{viii}	2.6756 (7)	Na2—S3^{iv}	3.055 (4)
Mo3—Mo3^{vii}	2.6756 (7)	Na2—Na2^{v}	3.397 (6)
Mo3—Mo2^{viii}	2.7081 (4)	Na2—Na2^{vi}	3.397 (6)
Mo3—Mo2^{x}	2.7081 (4)	Na2—Mo1^{xvii}	3.7042 (8)
Mo3—Mo2^{ix}	2.7303 (4)	Na1—S2^{xviii}	3.1669 (13)
Mo3—Na2^{iv}	2.896 (3)	Na1—S2^{iv}	3.1669 (13)
S1—Mo1^{iii}	2.4565 (9)	Na1—S2^{ii}	3.1669 (13)
S1—Mo1^{ii}	2.4830 (9)	Na1—S1^{iv}	3.3609 (19)
S1—Na1^{iv}	3.3609 (19)	Na1—S1^{xviii}	3.3609 (19)
S2—Mo2^{viii}	2.5070 (9)	Na1—S1^{ii}	3.3609 (19)
S4^{i}—Mo1—S1	171.81 (4)	Mo1—S1—Mo1^{ii}	66.65 (3)
S4^{i}—Mo1—S1^{ii}	90.83 (2)	Mo1^{iii}—S1—Mo1^{ii}	65.99 (3)
S1—Mo1—S1^{ii}	89.17 (2)	Mo1—S1—Mo2	134.06 (4)
S4^{i}—Mo1—S1^{iii}	90.20 (2)	Mo1^{iii}—S1—Mo2	130.92 (4)
S1—Mo1—S1^{iii}	88.56 (2)	Mo1^{ii}—S1—Mo2	82.94 (3)
S1^{ii}—Mo1—S1^{iii}	171.12 (4)	Mo1—S1—Na1^{iv}	127.79 (8)
S4^{i}—Mo1—S2^{iv}	93.04 (4)	Mo1^{iii}—S1—Na1^{iv}	97.39 (3)
S1—Mo1—S2^{iv}	95.15 (3)	Mo1^{ii}—S1—Na1^{iv}	153.45 (7)
S1^{ii}—Mo1—S2^{iv}	91.20 (3)	Mo2—S1—Na1^{iv}	94.64 (6)
S1^{iii}—Mo1—S2^{iv}	97.55 (3)	Mo2—S2—Mo3	66.88 (3)
S4^{i}—Mo1—Mo1^{v}	56.21 (2)	Mo2—S2—Mo2^{viii}	63.88 (2)
S1—Mo1—Mo1^{v}	116.82 (2)	Mo3—S2—Mo2^{viii}	65.76 (2)

S1^{ii}—Mo1—Mo1^{v}	117.37 (2)	Mo2—S2—Mo1^{iv}	129.13 (4)
S1^{iii}—Mo1—Mo1^{v}	56.53 (2)	Mo3—S2—Mo1^{iv}	132.33 (4)
S2^{iv}—Mo1—Mo1^{v}	135.73 (2)	Mo2^{viii}—S2—Mo1^{iv}	82.07 (3)
S4^{i}—Mo1—Mo1^{vi}	56.21 (2)	Mo2—S2—Na2^{iv}	133.09 (7)
S1—Mo1—Mo1^{vi}	117.46 (2)	Mo3—S2—Na2^{iv}	66.52 (6)
S1^{ii}—Mo1—Mo1^{vi}	57.48 (2)	Mo2^{viii}—S2—Na2^{iv}	100.94 (8)
S1^{iii}—Mo1—Mo1^{vi}	116.43 (2)	Mo1^{iv}—S2—Na2^{iv}	87.68 (6)
S2^{iv}—Mo1—Mo1^{vi}	131.85 (2)	Mo2—S2—Na1^{iv}	101.03 (3)
Mo1^{v}—Mo1—Mo1^{vi}	60.0	Mo3—S2—Na1^{iv}	122.15 (9)
S4^{i}—Mo1—Mo1^{iii}	116.37 (2)	Mo2^{viii}—S2—Na1^{iv}	160.14 (7)
S1—Mo1—Mo1^{iii}	56.60 (2)	Mo1^{iv}—S2—Na1^{iv}	100.15 (7)
S1^{ii}—Mo1—Mo1^{iii}	115.84 (3)	Na2^{iv}—S2—Na1^{iv}	98.88 (10)
S1^{iii}—Mo1—Mo1^{iii}	56.08 (2)	Mo3^{viii}—S3—Mo3	66.31 (4)
S2^{iv}—Mo1—Mo1^{iii}	138.14 (2)	Mo3^{viii}—S3—Na2^{xi}	157.19 (11)
Mo1^{v}—Mo1—Mo1^{iii}	60.241 (8)	Mo3—S3—Na2^{xi}	136.50 (11)
Mo1^{vi}—Mo1—Mo1^{iii}	90.0	Mo3^{viii}—S3—Mo2^{x}	65.57 (3)
S4^{i}—Mo1—Mo1^{ii}	116.37 (2)	Mo3—S3—Mo2^{x}	64.86 (3)
S1—Mo1—Mo1^{ii}	57.27 (2)	Na2^{xi}—S3—Mo2^{x}	119.39 (3)
S1^{ii}—Mo1—Mo1^{ii}	56.34 (2)	Mo3^{viii}—S3—Mo2^{viii}	65.57 (3)
S1^{iii}—Mo1—Mo1^{ii}	115.54 (3)	Mo3—S3—Mo2^{viii}	64.86 (3)
S2^{iv}—Mo1—Mo1^{ii}	134.12 (2)	Na2^{xi}—S3—Mo2^{viii}	119.39 (3)
Mo1^{v}—Mo1—Mo1^{ii}	90.0	Mo2^{x}—S3—Mo2^{viii}	119.89 (5)
Mo1^{vi}—Mo1—Mo1^{ii}	60.241 (8)	Mo3^{viii}—S3—Na2^{iv}	128.66 (8)
Mo1^{iii}—Mo1—Mo1^{ii}	59.518 (16)	Mo3—S3—Na2^{iv}	62.35 (7)
S4^{i}—Mo1—Na2	45.53 (6)	Na2^{xi}—S3—Na2^{iv}	74.15 (16)
S1—Mo1—Na2	142.51 (6)	Mo2^{x}—S3—Na2^{iv}	92.16 (5)
S1^{ii}—Mo1—Na2	83.36 (6)	Mo2^{viii}—S3—Na2^{iv}	92.16 (5)
S1^{iii}—Mo1—Na2	103.55 (6)	Mo1^{xii}—S4—Mo1^{xiii}	67.58 (5)
S2^{iv}—Mo1—Na2	48.59 (6)	Mo1^{xii}—S4—Mo1^{viii}	67.58 (5)
Mo1^{v}—Mo1—Na2	99.04 (6)	Mo1^{xiii}—S4—Mo1^{viii}	67.58 (5)
Mo1^{vi}—Mo1—Na2	88.97 (5)	Mo1^{xii}—S4—Na2^{xiii}	151.15 (7)
Mo1^{iii}—Mo1—Na2	156.07 (6)	Mo1^{xiii}—S4—Na2^{xiii}	93.82 (5)
Mo1^{ii}—Mo1—Na2	137.75 (5)	Mo1^{viii}—S4—Na2^{xiii}	127.12 (7)
S5—Mo2—S2	91.79 (2)	Mo1^{xii}—S4—Na2^{viii}	127.12 (7)
S5—Mo2—S2^{vii}	90.96 (2)	Mo1^{xiii}—S4—Na2^{viii}	151.15 (7)
S2—Mo2—S2^{vii}	172.09 (4)	Mo1^{viii}—S4—Na2^{viii}	93.82 (5)
S5—Mo2—S1	92.26 (3)	Na2^{xiii}—S4—Na2^{viii}	79.75 (9)
S2—Mo2—S1	89.86 (3)	Mo1^{xii}—S4—Na2^{xii}	93.82 (5)
S2^{vii}—Mo2—S1	97.44 (3)	Mo1^{xiii}—S4—Na2^{xii}	127.12 (7)
S5—Mo2—S3^{vii}	170.70 (4)	Mo1^{viii}—S4—Na2^{xii}	151.15 (7)
S2—Mo2—S3^{vii}	86.62 (4)	Na2^{xiii}—S4—Na2^{xii}	79.75 (9)
S2^{vii}—Mo2—S3^{vii}	89.47 (4)	Na2^{viii}—S4—Na2^{xii}	79.75 (9)
S1—Mo2—S3^{vii}	96.89 (3)	Mo2^{viii}—S5—Mo2	66.48 (4)
S5—Mo2—Mo2^{vii}	56.76 (2)	Mo2^{viii}—S5—Mo2^{vii}	66.48 (4)
S2—Mo2—Mo2^{vii}	118.56 (2)	Mo2—S5—Mo2^{vii}	66.48 (4)
S2^{vii}—Mo2—Mo2^{vii}	57.44 (2)	Mo2^{viii}—S5—Na1	140.73 (3)
S1—Mo2—Mo2^{vii}	136.00 (2)	Mo2—S5—Na1	140.73 (3)
S3^{vii}—Mo2—Mo2^{vii}	116.29 (3)	Mo2^{vii}—S5—Na1	140.73 (3)
S5—Mo2—Mo2^{viii}	56.76 (2)	S3^{xiv}—Na2—S4^{i}	89.92 (9)

S2—Mo2—Mo2^{viii}	58.68 (2)	S3^{xiv}—Na2—S4^{xv}	89.92 (9)
S2^{vii}—Mo2—Mo2^{viii}	117.32 (2)	S4^{i}—Na2—S4^{xv}	84.49 (12)
S1—Mo2—Mo2^{viii}	131.42 (2)	S3^{xiv}—Na2—S2^{xvi}	112.74 (10)
S3^{vii}—Mo2—Mo2^{viii}	115.08 (3)	S4^{i}—Na2—S2^{xvi}	154.21 (15)
Mo2^{vii}—Mo2—Mo2^{viii}	60.0	S4^{xv}—Na2—S2^{xvi}	83.46 (4)
S5—Mo2—Mo3^{vii}	118.14 (2)	S3^{xiv}—Na2—S2^{iv}	112.74 (10)
S2—Mo2—Mo3^{vii}	115.63 (3)	S4^{i}—Na2—S2^{iv}	83.46 (4)
S2^{vii}—Mo2—Mo3^{vii}	56.66 (2)	S4^{xv}—Na2—S2^{iv}	154.21 (15)
S1—Mo2—Mo3^{vii}	137.83 (3)	S2^{xvi}—Na2—S2^{iv}	97.94 (11)
S3^{vii}—Mo2—Mo3^{vii}	54.99 (3)	S3^{xiv}—Na2—Mo3^{iv}	145.61 (16)
Mo2^{vii}—Mo2—Mo3^{vii}	61.444 (11)	S4^{i}—Na2—Mo3^{iv}	114.79 (9)
Mo2^{viii}—Mo2—Mo3^{vii}	90.670 (10)	S4^{xv}—Na2—Mo3^{iv}	114.79 (9)
S5—Mo2—Mo3	117.29 (2)	S2^{xvi}—Na2—Mo3^{iv}	51.78 (6)
S2—Mo2—Mo3	56.69 (2)	S2^{iv}—Na2—Mo3^{iv}	51.78 (6)
S2^{vii}—Mo2—Mo3	115.55 (3)	S3^{xiv}—Na2—S3^{iv}	165.85 (15)
S1—Mo2—Mo3	133.65 (3)	S4^{i}—Na2—S3^{iv}	79.65 (9)
S3^{vii}—Mo2—Mo3	54.52 (3)	S4^{xv}—Na2—S3^{iv}	79.65 (9)
Mo2^{vii}—Mo2—Mo3	90.184 (10)	S2^{xvi}—Na2—S3^{iv}	75.81 (8)
Mo2^{viii}—Mo2—Mo3	60.600 (11)	S2^{iv}—Na2—S3^{iv}	75.81 (8)
Mo3^{vii}—Mo2—Mo3	58.940 (16)	Mo3^{iv}—Na2—S3^{iv}	48.54 (6)
S3^{vii}—Mo3—S3	173.69 (4)	S3^{xiv}—Na2—Na2^{v}	119.90 (13)
S3^{vii}—Mo3—S2^{ix}	89.88 (3)	S4^{i}—Na2—Na2^{v}	50.13 (5)
S3—Mo3—S2^{ix}	93.48 (3)	S4^{xv}—Na2—Na2^{v}	50.13 (5)
S3^{vii}—Mo3—S2	89.88 (3)	S2^{xvi}—Na2—Na2^{v}	105.50 (12)
S3—Mo3—S2	93.48 (3)	S2^{iv}—Na2—Na2^{v}	105.50 (12)
S2^{ix}—Mo3—S2	115.45 (4)	Mo3^{iv}—Na2—Na2^{v}	94.49 (15)
S3^{vii}—Mo3—Mo3^{viii}	117.00 (4)	S3^{iv}—Na2—Na2^{v}	45.95 (11)
S3—Mo3—Mo3^{viii}	56.69 (4)	S3^{xiv}—Na2—Na2^{vi}	59.90 (13)
S2^{ix}—Mo3—Mo3^{viii}	118.47 (2)	S4^{i}—Na2—Na2^{vi}	50.13 (5)
S2—Mo3—Mo3^{viii}	118.47 (2)	S4^{xv}—Na2—Na2^{vi}	50.13 (5)
S3^{vii}—Mo3—Mo3^{vii}	57.00 (4)	S2^{xvi}—Na2—Na2^{vi}	130.76 (6)
S3—Mo3—Mo3^{vii}	116.69 (4)	S2^{iv}—Na2—Na2^{vi}	130.76 (6)
S2^{ix}—Mo3—Mo3^{vii}	116.54 (2)	Mo3^{iv}—Na2—Na2^{vi}	154.49 (15)
S2—Mo3—Mo3^{vii}	116.54 (2)	S3^{iv}—Na2—Na2^{vi}	105.95 (11)
Mo3^{viii}—Mo3—Mo3^{vii}	60.0	Na2^{v}—Na2—Na2^{vi}	60.0
S3^{vii}—Mo3—Mo2^{viii}	117.827 (15)	S3^{xiv}—Na2—Mo1	97.96 (5)
S3—Mo3—Mo2^{viii}	60.149 (14)	S4^{i}—Na2—Mo1	40.65 (3)
S2^{ix}—Mo3—Mo2^{viii}	150.01 (3)	S4^{xv}—Na2—Mo1	124.10 (12)
S2—Mo3—Mo2^{viii}	57.58 (2)	S2^{xvi}—Na2—Mo1	139.27 (11)
Mo3^{viii}—Mo3—Mo2^{viii}	60.944 (12)	S2^{iv}—Na2—Mo1	43.72 (2)
Mo3^{vii}—Mo3—Mo2^{viii}	89.804 (10)	Mo3^{iv}—Na2—Mo1	87.79 (5)
S3^{vii}—Mo3—Mo2^{x}	117.827 (15)	S3^{iv}—Na2—Mo1	80.39 (5)
S3—Mo3—Mo2^{x}	60.149 (14)	Na2^{v}—Na2—Mo1	79.33 (6)
S2^{ix}—Mo3—Mo2^{x}	57.58 (2)	Na2^{vi}—Na2—Mo1	87.34 (5)
S2—Mo3—Mo2^{x}	150.01 (3)	S3^{xiv}—Na2—Mo1^{xvii}	97.96 (5)
Mo3^{viii}—Mo3—Mo2^{x}	60.944 (12)	S4^{i}—Na2—Mo1^{xvii}	124.10 (12)
Mo3^{vii}—Mo3—Mo2^{x}	89.804 (10)	S4^{xv}—Na2—Mo1^{xvii}	40.65 (3)
Mo2^{viii}—Mo3—Mo2^{x}	112.05 (2)	S2^{xvi}—Na2—Mo1^{xvii}	43.72 (2)
S3^{vii}—Mo3—Mo2^{ix}	59.911 (14)	S2^{iv}—Na2—Mo1^{xvii}	139.27 (11)

$S3—Mo3—Mo2^{ix}$	117.957 (16)
$S2^{ix}—Mo3—Mo2^{ix}$	56.42 (2)
$S2—Mo3—Mo2^{ix}$	146.91 (3)
$Mo3^{viii}—Mo3—Mo2^{ix}$	89.333 (10)
$Mo3^{vii}—Mo3—Mo2^{ix}$	60.116 (12)
$Mo2^{viii}—Mo3—Mo2^{ix}$	146.475 (18)
$Mo2^{x}—Mo3—Mo2^{ix}$	57.956 (12)
$S3^{vii}—Mo3—Mo2$	59.911 (14)
$S3—Mo3—Mo2$	117.957 (16)
$S2^{ix}—Mo3—Mo2$	146.91 (3)
$S2—Mo3—Mo2$	56.42 (2)
$Mo3^{viii}—Mo3—Mo2$	89.333 (10)
$Mo3^{vii}—Mo3—Mo2$	60.116 (12)
$Mo2^{viii}—Mo3—Mo2$	57.956 (12)
$Mo2^{x}—Mo3—Mo2$	146.475 (18)
$Mo2^{ix}—Mo3—Mo2$	110.679 (19)
$S3^{vii}—Mo3—Na2^{iv}$	117.20 (8)
$S3—Mo3—Na2^{iv}$	69.11 (8)
$S2^{ix}—Mo3—Na2^{iv}$	61.70 (3)
$S2—Mo3—Na2^{iv}$	61.70 (3)
$Mo3^{viii}—Mo3—Na2^{iv}$	125.80 (8)
$Mo3^{vii}—Mo3—Na2^{iv}$	174.20 (8)
$Mo2^{viii}—Mo3—Na2^{iv}$	93.43 (4)
$Mo2^{x}—Mo3—Na2^{iv}$	93.43 (4)
$Mo2^{ix}—Mo3—Na2^{iv}$	117.90 (3)
$Mo2—Mo3—Na2^{iv}$	117.90 (3)
$Mo1—S1—Mo1^{iii}$	67.06 (3)
$Mo3^{iv}—Na2—Mo1^{xvii}$	87.79 (5)
$S3^{iv}—Na2—Mo1^{xvii}$	80.39 (5)
$Na2^{v}—Na2—Mo1^{xvii}$	79.33 (6)
$Na2^{vi}—Na2—Mo1^{xvii}$	87.34 (5)
$Mo1—Na2—Mo1^{xvii}$	157.78 (11)
$S5—Na1—S2^{xviii}$	100.69 (9)
$S5—Na1—S2^{iv}$	100.69 (9)
$S2^{xviii}—Na1—S2^{iv}$	116.64 (6)
$S5—Na1—S2^{ii}$	100.69 (9)
$S2^{xviii}—Na1—S2^{ii}$	116.64 (6)
$S2^{iv}—Na1—S2^{ii}$	116.64 (6)
$S5—Na1—S1^{iv}$	71.10 (8)
$S2^{xviii}—Na1—S1^{iv}$	66.58 (2)
$S2^{iv}—Na1—S1^{iv}$	65.67 (2)
$S2^{ii}—Na1—S1^{iv}$	171.77 (17)
$S5—Na1—S1^{xviii}$	71.10 (8)
$S2^{xviii}—Na1—S1^{xviii}$	65.67 (2)
$S2^{iv}—Na1—S1^{xviii}$	171.77 (17)
$S2^{ii}—Na1—S1^{xviii}$	66.58 (2)
$S1^{iv}—Na1—S1^{xviii}$	110.03 (8)
$S5—Na1—S1^{ii}$	71.10 (8)
$S2^{xviii}—Na1—S1^{ii}$	171.77 (17)
$S2^{iv}—Na1—S1^{ii}$	66.58 (2)
$S2^{ii}—Na1—S1^{ii}$	65.67 (2)
$S1^{iv}—Na1—S1^{ii}$	110.03 (8)
$S1^{xviii}—Na1—S1^{ii}$	110.03 (8)

Symmetry codes: (i) $x+1, y, z$; (ii) $x-y, x-1, -z$; (iii) $y+1, -x+y+1, -z$; (iv) $-x+1, -y, -z$; (v) $-x+y+2, -x+1, z$; (vi) $-y+1, x-y-1, z$; (vii) $-x+y+1, -x, z$; (viii) $-y, x-y-1, z$; (ix) $x, y, -z+1/2$; (x) $-y, x-y-1, -z+1/2$; (xi) $x-y-1, x-1, -z$; (xii) $-x+y+1, -x+1, z$; (xiii) $x-1, y, z$; (xiv) $y+1, -x+y, -z$; (xv) $x+1, y, -z-1/2$; (xvi) $-x+1, -y, z-1/2$; (xvii) $x, y, -z-1/2$; (xviii) $y, -x+y, -z$.